PB86-169935

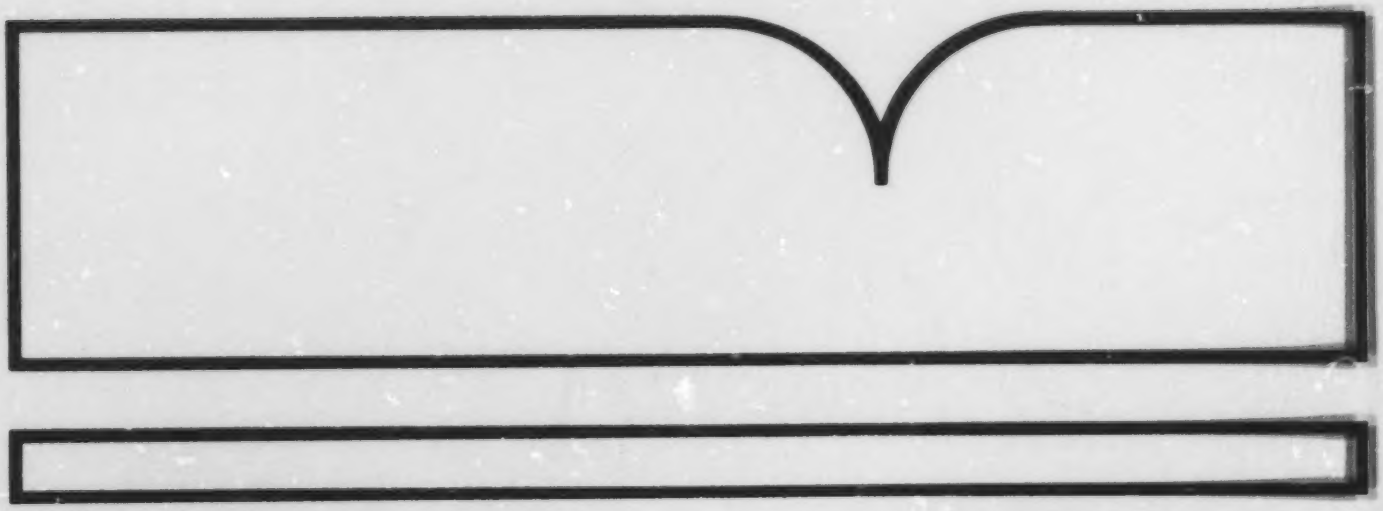
Transport of Organic Contaminants in Groundwater: Distribution and Fate of Chemicals in Sand and Gravel Aquifers

Stanford Univ., CA

Prepared for

Robert S. Kerr Environmental Research Lab.
Ada, OK

1985



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1. REPORT NO. EPA/600/J-85/339	2.	3. RECI PB86-169935
4. TITLE AND SUBTITLE TRANSPORT OF ORGANIC CONTAMINANTS IN GROUNDWATER Distribution and fate of chemicals in sand and gravel aquifers. (Journal Version)		5. REPORT DATE 1985 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Douglas M. Mackay John A. Cherry Paul V. Roberts		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Dept. Civil Engineering Stanford University Stanford, CA 94305 Dept. Earth Sciences University of Waterloo Waterloo, Ontario N2L 3G1 CANADA		10. PROGRAM ELEMENT NO. CBWD1A 11. CONTRACT/GRANT NO. CR-808851
12. SPONSORING AGENCY NAME AND ADDRESS Robert S. Kerr Environmental Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Ada, Oklahoma 74820		13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA/600/15

15. SUPPLEMENTARY NOTES

Published in JOURNAL OF ENVIRONMENTAL SCIENCE AND TECHNOLOGY, 19(5):384-392, May 1985.

16. ABSTRACT

The state-of-knowledge of the physical, chemical, and biological processes that are thought to affect organic contaminants in ground water are reviewed. The discussion is confined to horizontal flow in uniform sand and gravel aquifers. General principles governing contaminant transport are used to illustrate the conceptual complexities of organic chemical transport in ground water. Finally, the implications of ground-water contamination are discussed.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC.	UNCLASSIFIED	11
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

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EPA/600/J-85/339
JOURNAL ARTICLE

ES&T
CRITICAL REVIEW

Transport of organic contaminants in groundwater

Distribution and fate of chemicals in sand and gravel aquifers

Douglas M. Mackay
Paul V. Roberts
Department of Civil Engineering
Stanford University
Stanford, Calif. 94305

John A. Cherry
Department of Earth Sciences
University of Waterloo
Waterloo, Ontario N2L 3G1 Canada

Frequent discoveries of groundwater contamination arising from use, storage, and disposal of hazardous chemicals underscore the need for an understanding of and ultimately the ability to predict the mechanisms of transport of contaminants in the subsurface. In particular, there has been a tremendous interest in developing computerized contaminant transport models, and many such models have been documented (*1*).

The ability to develop mathematical formulations of a problem that is not directly observable and the ease with which models can be used to predict contaminant migration have led to their widespread acceptance as important tools in the investigation of groundwater contamination in sand and gravel aquifers. However, it is critical to keep in mind that the strength of available models is directly related to the depth of present understanding of the fundamental processes that control the transport and fate of contaminants.

In this article we review the state of understanding of the physical, chemical, and biological processes that are thought to affect organic contaminants in the saturated (groundwater) zone. Although contaminants that enter the saturated zone often must first pass through the unsaturated (vadose) zone, we do not discuss that zone in any detail. Because many aquifers used for water supply comprise horizontal geological units of sand and gravel, we confine our discussion to horizontal flow in such aquifers. Our purpose is to draw on the current understanding of the processes that are important to the saturated zone. This will help to illustrate the conceptual complexities of organic contaminant transport and distribution in the groundwater zone. Finally, we present some of the implications of groundwater contamination.

Transport processes

Organic contaminants can reach the groundwater zone either dissolved in water or as organic liquid phases that may be immiscible in water. Dissolved contaminants can result from spills or leaks of aqueous solutions or from the leaching of solid phases or immiscible organic liquids present in the vadose zone or land disposal areas. Organic liquids can be introduced to the subsurface by spills, leaks, or intentional disposal.

The subsurface transport of immiscible organic liquids is governed by a set of factors different from those for dissolved contaminants. However, some components of organic liquids can dissolve into the groundwater. Therefore, in the following synoptic discussion, we begin with the processes that most strongly influence the migration of dissolved organic solutes.

Advection

In sand and gravel aquifers, the dominant factor in the migration of a dissolved contaminant is advection, the process by which solutes are transported by the bulk motion of flowing groundwater. Groundwater generally flows from regions of the subsurface where water level is high to regions where water level is low. Hydraulic gradient is the term used to describe the magnitude of this driving force. The average linear velocity at which groundwater flows through a granular medium, such as a sand and gravel aquifer, is equal to the product of the gradient and the inherent capability of the medium to transmit water. The latter is expressed as the ratio of the medium's hydraulic conductivity and porosity (*2*).

For uniform sand and gravel aquifers in gentle topography, the gradient normally follows the topography, and the groundwater flow rate can be estimated to within a factor of 10, given a general description of the geologic medium. More accurate estimates are possible if site-specific measurements of aquifer properties are available. Groundwater velocities in such aquifers typically range between 1 meter/year (m/y) and 1000 m/y. In most cases, however, the flow velocities under natural gradient conditions are probably between 10 m/y and 100 m/y. Thus, when monitoring wells or small supply wells in sand and gravel aquifers are located hundreds or thousands of meters downgradient of a contaminant source, the average travel time for the groundwater to flow from source to well typically is on the order of decades. In the zone of influence of a high-capacity well or wellfield, however, the artificially increased gradient substantially increases the local velocity, and the average travel times for groundwater flow are reduced.

Dispersion

Dissolved contaminants spread as they move with the groundwater. This process, called dispersion, results from two basic processes, molecular diffusion and mechanical mixing. The kinetic activity of dissolved solutes results in the net flux, or diffusion, of

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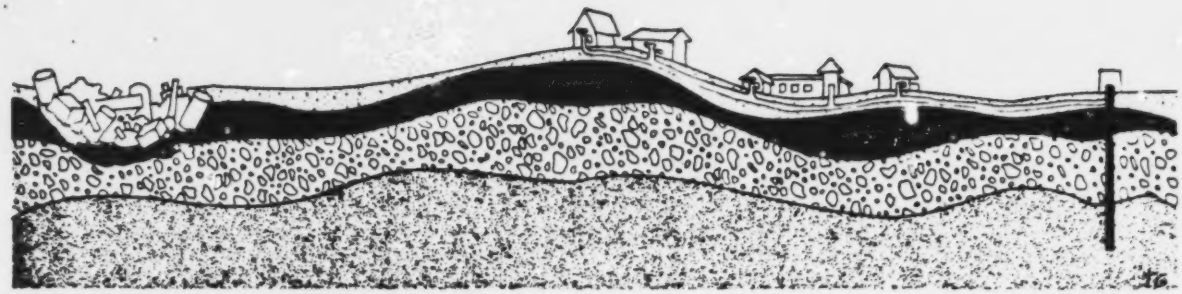


the solutes from a zone of high concentration to a zone of lower concentration. Mechanical mixing results from variations in groundwater velocity within the porous aquifer caused by frictional forces, variations in pore geometry, and fluctuations in the local flow directions relative to the mean flow direction.

Dispersion and spreading during transport result in the dilution of contaminant pulses and the attenuation of concentration peaks; the maximum concentrations diminish with increasing distance from the source. In plumes containing irregular concentration distributions, this spreading will lead to an increase in plume uniformity with distance. In addition, dispersive spreading may result in the arrival of detectable contaminant concentrations at a given location significantly before the arrival time that is expected solely on the basis of the average groundwater flow rate.

Despite the practical importance of the dispersion process, there is currently no method to confidently predict the magnitude of dispersion for a previously unstudied field situation. For simple hydrogeological systems, the spreading is believed to be proportional to the flow rate. For more complex systems, the constant of proportionality—termed the dispersivity—appears to depend on the structure of the geologic medium in such a manner that it varies with the distance traversed (*3, 4*). Furthermore, dispersion in the direction of flow often is observed to be markedly greater than dispersion in the directions transverse to the flow. Although very little is known about vertical transverse dispersivity, past field work on aquifers of sedimentary origin indicates that the ratio of apparent dispersivities in the longitudinal and horizontal transverse directions typically ranges from 10 to 100 (*3, 4*).

In the absence of detailed studies to determine the dispersive characteristics of a given field situation, longitudinal and transverse dispersivities must be estimated based on prior field work in similar hydrogeological systems. Given the current level of understanding, such estimates are characterized by a high degree of uncertainty. For example, longitudinal dispersivity values inferred from past field efforts range over approximately one order of magnitude when they are compared for a given transport distance (*3*). Furthermore, for many problems pertaining to plume development and extent, continuing research suggests that dispersion in the transverse directions—about which we know even less—is of more practical importance.

Sorption and retardation

Some dissolved contaminants may interact with the aquifer solids encountered along the flow path through adsorption, partitioning, ion exchange, and other processes (*2*). These interactions result in the contaminants' distribution between the aqueous phase and the aquifer solids, diminution of concentrations in the aqueous phase, and retardation of the movement of the contaminant relative to groundwater flow (*5–8*). The higher the fraction of the contaminant sorbed, the more retarded is its transport.

For some contaminants, such as ionic species of heavy metals (cadmium, chromium, etc.) and certain organic solutes, the degree of interaction depends on many factors. These include the concentration and characteristics of the contaminant, the characteristics of the aquifer solids, the pH of the groundwater, and the presence of other dissolved constituents (*9–11*). It is possible for the degree of interaction, and therefore retardation, to vary in space and time due to variations in one or more of these factors in the natural groundwater environment (*10, 11*). Complexities such as these confound the prediction of groundwater transport of such contaminants.

In the case of some groundwater contaminants, such as certain halogenated organic solvents, the interaction, called sorption, is often affected in a significant way by only two factors: the contaminant's hydrophobility (its antipathy to dissolving in water) and the fraction of solid organic matter in the aquifer solids (organic carbon content) (*9*). In a homogeneous aquifer, therefore, sorption of a hydrophobic organic solute should theoretically be constant in space and time. If the sorptive interaction is at equilibrium and completely reversible, the solute should move at a constant average velocity equal to the groundwater's average velocity, divided by the "retardation factor." Such a contaminant is said to be linearly retarded.

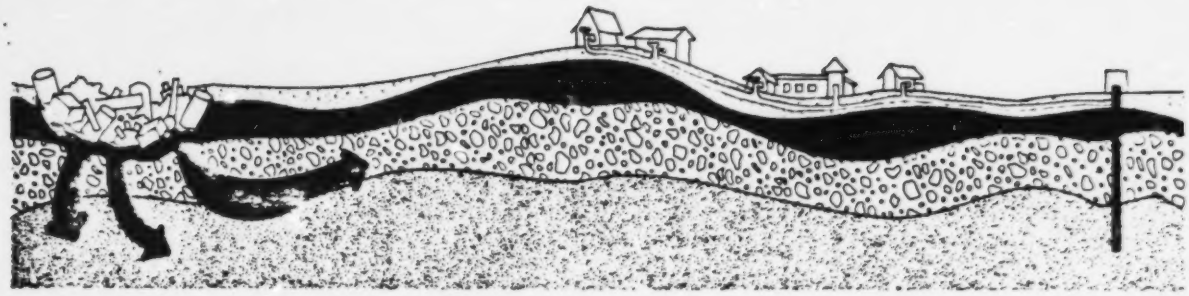
More hydrophobic compounds should be more highly retarded, a trend observed in several field studies (*12–14*). Roberts et al. show that retardation factors for hydrophobic organic contaminants of concern can be expected to range over four orders of magnitude, from slightly greater than one to as much as 10,000 (*15*). Among the most common groundwater contaminants are carbon tetrachloride, 1,1,1-trichloroethane (TCA), trichloroethylene (TCE), and tetrachloroethylene (perchloroethylene, PCE) (*16*). The retardation factors for these compounds are expected to fall in a range from 1 to 10 for many sand and gravel aquifers that are low in solid organic matter. Thus, in many aquifers used for water supply these contaminants would be expected to migrate at rates from 10% to nearly 100% of the velocity of the groundwater itself.

As mentioned above, however, the simple hydrophobic sorption and retardation model may not be applicable in all cases. For example, sorption by mineral surfaces may approach or exceed that by the solid organic matter if the ratio of mineral surface area to organic matter content is large (*9, 17*). In addition, there is evidence that in some cases sorption equilibrium may require weeks or months and thus may not always be reached in the field (*9*).

Variability of aquifer properties and interaction between sorption and other processes also may confound the application of the simple retardation concepts. For example, in heterogeneous sand and gravel aquifers the highest hydraulic conductivity zones may have the least solid organic matter. In such a case, the lowest retardation of hydrophobic organic contaminants would occur in the zones of fastest groundwater flow. Predictions of contaminant migration that do not account for this hydrogeologic heterogeneity can be significantly in error.

Chemical, biological transformation

Organic contaminants can be transformed into other compounds by an ex-



traordinarily complex set of chemical and biological mechanisms. The effects, relative importance, and interactions of these processes in the groundwater zone, which are not well understood, are increasingly the subject of research.

The principal classes of chemical reactions that can affect organic contaminants in water are hydrolysis and oxidation (*18*). Although empirical methods have been developed to estimate the rate constants for the effects of both processes on particular contaminants under specific solution conditions, the applicability of these methods to reactions in the groundwater zone is unknown. It is believed, however, that most chemical reactions occurring in the groundwater zone are likely to be slow compared with transformations mediated by microorganisms (*19, 20*).

There is good evidence that certain organic groundwater contaminants can be biologically transformed by microorganisms attached to solid surfaces within the aquifer (*19*). The attached bacteria obtain energy and nutrients from the groundwater flowing by and may form biofilms as their numbers increase. Energy for growth is obtained from oxidation of organic substrates or inorganic compounds, such as hydrogen or reduced forms of iron, nitrogen, or sulfur (*19*). Microorganisms vary in their ability to use the different electron acceptors required for these oxidations: Some use oxygen available under aerobic groundwater conditions. Others may use nitrate, sulfate, or carbon dioxide when conditions are anoxic (*19*).

There are many factors affecting the rates of biotransformation of organic compounds, including water temperature and pH, the number and species of microorganisms present, the concentration of the substrate, the presence of microbial toxicants and nutrients, and the availability of electron acceptors (*21*). In some cases, the native microflora may not be able to transform a specific compound, or may manifest that ability only after a considerable period of acclimation. It is not yet known whether deep aquifers generally contain sufficient numbers of bacteria to achieve substantial biotransformation rates of organic contaminants, but Wilson and McNabb have found surprisingly high numbers of bacteria in shallow, unconfined aquifers at depths of 6 m or less (*22*).

There is a minimum concentration to which a single substrate can be decomposed under steady-state conditions. Below this level there is insufficient energy available to support continued bacterial growth (*21*). Biodegradable organic contaminants often are present at trace concentrations below the minimum level. In such cases biotransformation of the contaminants can occur if they are used as secondary substrates, but this requires the presence of an abundant primary substrate (or combination of degradable primary substrates) and bacteria that are able to transform both primary and secondary substrates (*21*).

It is widely believed that biotransformation of trace organic contaminants can and does occur in the groundwater zone under some conditions, sometimes after acclimation periods of months or years. The rates are believed to range widely, with half-lives ranging from a few days to many years, and may be significant in light of the low groundwater flow rates and long residence times that characterize aquifers (*21*).

Nonetheless, transformation of a toxic organic solute is no assurance that it has been converted to harmless or even less hazardous products. Biotransformation of common groundwater contaminants, such as PCE, TCE, and TCA, can result in the formation of such intermediates as vinyl chloride, which cannot be further transformed under prevailing conditions (*21*). Given our limited understanding of transformation processes and the factors influencing them, prudence dictates that in forecasting the effects of groundwater contamination, hazardous contaminants must be assumed, in the absence of site-specific evidence to the contrary, to persist indefinitely.

Immiscible organic liquids

Organic compounds differ widely in their solubility, from infinitely miscible polar compounds, such as methanol, to extremely low solubility nonpolar compounds, such as polynuclear aromatic hydrocarbons (*23*). Commonly encountered groundwater contaminants, including halogenated aliphatics with one or two carbon atoms, tend to have moderately low solubilities (< 1%). Thus many organic liquids released to the subsurface may migrate as discrete nonaqueous phases, some components of which may dissolve into the surrounding groundwater. The migration of an immiscible organic liquid phase in the subsurface is governed largely by its density and viscosity.

Density differences of about 1% are known to influence fluid movement significantly in the subsurface environment. For example, the stratification of saltwater and freshwater occurs at a density difference of 3.5%. With few exceptions, the densities of organic liquids differ from that of water by more than 1%. In most cases the difference is more than 10%. The specific gravities of hydrocarbons (gasoline and other petroleum distillates) may be as low as 0.7, and halogenated hydrocarbons are almost without exception significantly more dense than water. Chlorinated aliphatic compounds containing one- and two-carbon atoms have specific gravities from 1.2 to 1.5.

It is convenient to consider organic liquids less dense than water as "floaters," which spread across the water table, and organic liquids more dense than water as "sinkers," which may plummet through sand and gravel aquifers to the underlying aquitard (relatively impermeable layers) where present. There is extensive evidence from field studies that low-density organic liquids float on the water table (*24*). The sinking phenomenon has been demonstrated in physical model experiments by Schwille (*25*), and some corroborative evidence has been found in field observations of the spatial distribution of contaminants near landfills and other sources (*26*). It is important to recognize that the migration of dense organic liquids is largely uncoupled from the hydraulic gradient that drives advective transport and that the movement may have a dominant vertical component even in horizontally flowing aquifers.

The transport of an organic liquid phase also is influenced by its viscosity

and its surface-wetting properties compared with those of water. Schwille has shown that halogenated aliphatics tend to spread by capillary action into aquifer media and that they tend to be retained in amounts of about 0.3% to 5% by volume, following the passage of the organic liquid (25). This points to the possibility of storage of large quantities of immiscible liquid organic contaminants as droplets dispersed within the pores of aquifer media, even if the bulk of the migrating mass of liquid is removed. The organic liquid droplets retained in the aquifer may then dissolve over time into the groundwater flowing past them.

An organic liquid of moderately low solubility (such as PCE) can contaminate as much as 10,000 times its own volume to its solubility limit. However, organic compounds are only rarely found in groundwater at concentrations approaching their solubility limits, even when organic liquid phases are known or suspected to be present. The observed concentrations are usually more than a factor of 10 lower than the solubility, presumably because of the diffusional limitations of dissolution and the dilution of the dissolved organic contaminants by dispersion. This implies that the volume of groundwater that could be contaminated by an organic liquid phase is much larger than that calculated by assuming dissolution to the solubility limit. It is evident that what might once have been considered a small spill or leak (for example, tens of gallons of a pure industrial solvent spilled every time a tank is filled or a transfer line is flushed) may in fact constitute a significant source of contamination if the spilled liquid reaches the groundwater zone.

Transport and distribution

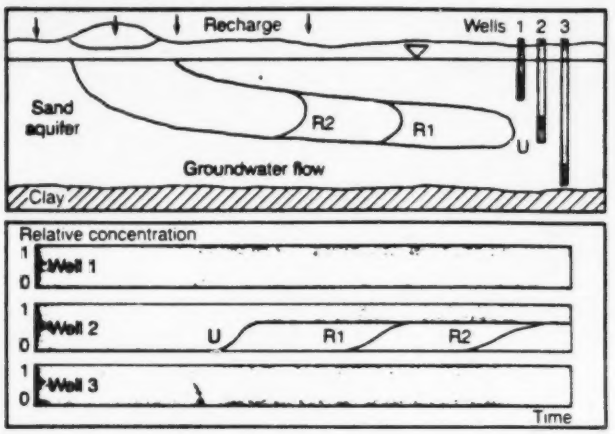
After discussing the processes that affect organic contaminant transport in the subsurface, it is worthwhile to consider illustrations of their effects in the conceptually simplest hydrogeologic domain: a uniform, unconfined sandy aquifer underlain by a level horizontal aquitard. We will assume that the water table is close to the surface and that the hazardous organic chemicals have been released directly into the sand by a spill or leak or by the leaching of materials deposited in an unlined dump.

Continuous sources

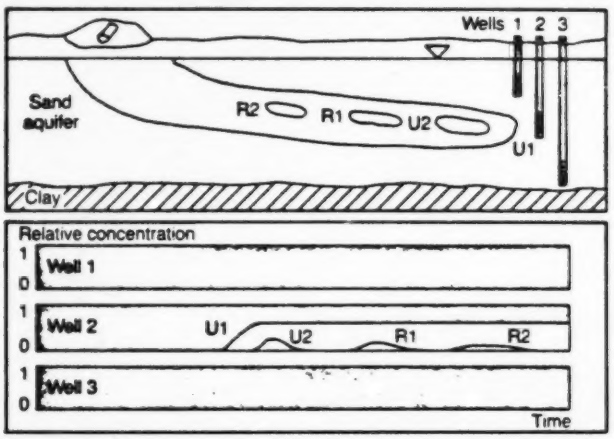
Figure 1a illustrates a case in which hazardous chemicals are distributed uniformly in a waste mass or contaminated soil zone and are leached slowly by precipitation. We assume that the aqueous leachate is relatively uniform in composition and flow over many years (implying a large reservoir of

FIGURE 1
Contamination from various sources in an unconfined aquifer[a]

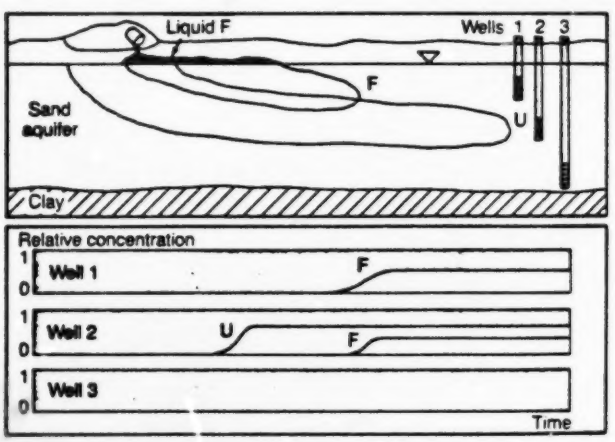
(a) Continuous source of three dissolved contaminants; unretarded (U) and retarded to varying degrees (R1, R2)



(b) Continuous source of a dissolved, unretarded contaminant (U1) and a pulse source of three dissolved contaminants; unretarded (U2) and retarded (R1, R2)



(c) Continuous source of a dissolved, unretarded contaminant (U) and a pulse source of an organic liquid (F) that floats on and slowly dissolves into the groundwater



[a]Top frames show contaminant distribution at one point in time. Bottom frames show concentration history at each well. Relative concentration expresses the observed value as a fraction of the undiluted leachate (U1, U2, R1, R2), contaminant solubility (F, S), or parent compound concentration (SS)

leachable contaminants). We also assume that the leachate contains nonsorbing, unretarded contaminants (U), such as chloride ions, and two contaminants that are linearly retarded to varying degrees (R1 and R2). Examples might be TCE and PCE.

Figure 1a shows the expected contaminant distributions at one point in time and the contaminant concentration histories observed in three monitoring wells screened at different depths. Intermittent pumping of the wells is assumed to withdraw minor amounts of water and does not influence plume migration. The vertical gradient, owing to natural recharge or density effects, results in the contaminants being observed in Well 2 only. It is also apparent that the contaminants arrive at the well at different times because the plume from the source is not spatially uniform, even in this simple case, but actually is composed of three overlapping plumes migrating at different rates.

The concentrations of all contaminants observed in Well 2 rise to levels below those of the undiluted leachate. The gradual rise is the result of dispersion (primarily longitudinal) of the advancing front. The reduction in maximum concentration below the undiluted value is because of dispersion in the transverse directions.

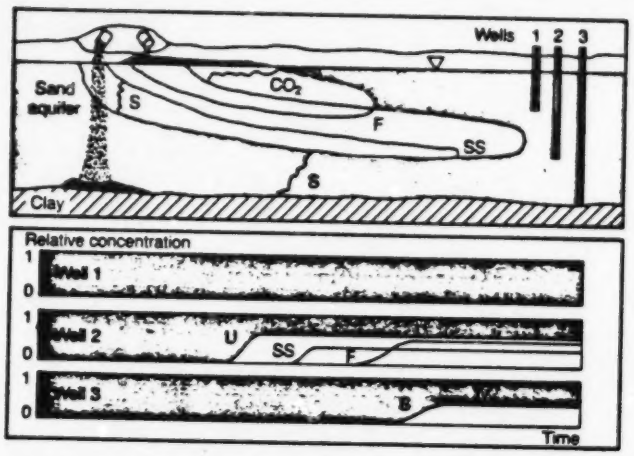
Pulse sources

A different case is illustrated in Figure 1b. Here we assume that a mass of uniform bulk waste produces aqueous leachate that is uniform in flow and composition but contains only nonsorbing contaminants (U1). This bulk waste contains a local source that releases a slug containing three contaminants (one is conservative and two are linearly retarded—U2, R1, and R2, respectively) shortly after leaching of the bulk waste begins. The release could be the result of the sudden rupture of a buried drum (due to corrosion or compaction), leaching of a localized contaminant source over a relatively short time (from a load of contaminated soil), or disposal of a tank load of an aqueous solution of contaminants.

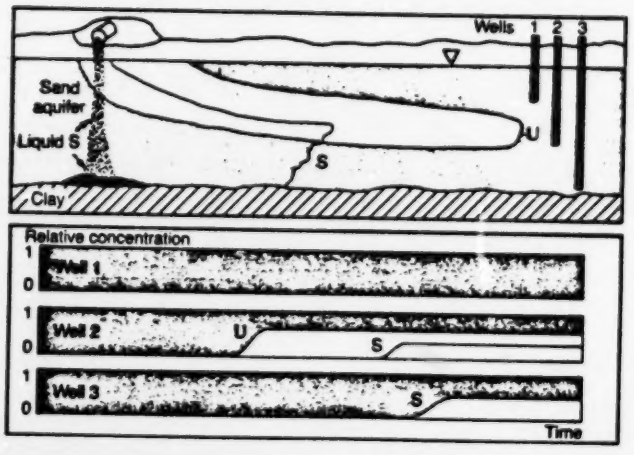
Figure 1b shows contaminant pulses migrating within the larger plume emanating from the bulk waste. Note that the pulses lengthen with distance, because of dispersion. As before, only Well 2 is affected, but the concentration history at the well is different. Contaminants U2, R1, and R2 affect the monitoring well for finite periods that depend on the duration and size of the source and the advective–dispersive characteristics of the aquifer. Note also that dispersion of the pulse of conservative contaminant U2 will reduce its peak concentration observed at Well 2 to substantially below that of the undiluted initial slug. For the retarded contaminants, both dispersion and sorption serve to reduce the observed peak solution concentrations.

FIGURE 1 (continued)

(d) Continuous source of a dissolved, unretarded contaminant (U) and a pulse source of an organic liquid (S) that sinks through and slowly dissolves into the groundwater



(e) Continuous source of dissolved, unretarded solutes (U) and two pulse sources: floater (F) and sinker (S). The aquifer is aerobic except within the anaerobic U plume. Dissolved F degrades aerobically to CO_2 and water. Dissolved S degrades anaerobically to by-product SS, which is not readily degraded and is less retarded than S or F



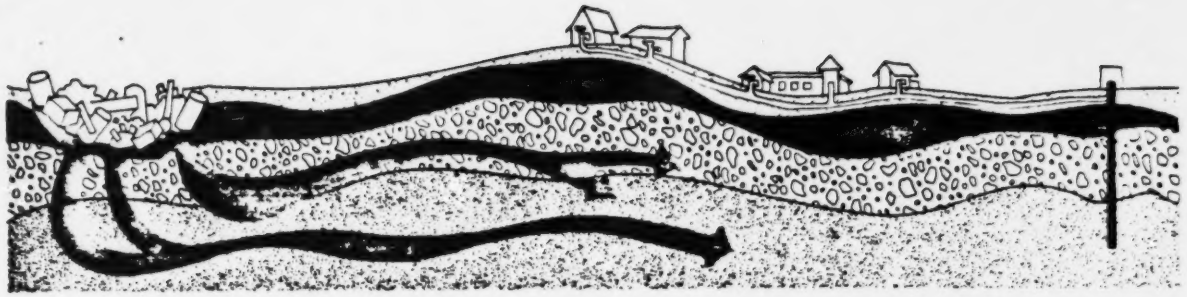
Low-density organic liquids

Suppose now that there is a similar situation, except that the local source within the bulk waste creates a release of an organic liquid contaminant, such as gasoline, that is immiscible with and less dense than the groundwater. In this case, the organic liquid migrates vertically to and then floats on the water table, spreading out in the downgradient direction. If the organic liquid contains contaminant F (e.g., benzene), which is slightly soluble in water, a plume will develop in the saturated zone.

Figure 1c shows the overlapping plumes that might result. It also shows that the dissolving contaminant might affect both of the shallow wells, depending on the size of the source and the degree to which the organic liquid spreads as it floats on the water table. The dissolved contaminant F is assumed to be slightly retarded during transport in the saturated zone. The concentration of F observed in the wells is likely to be considerably lower than its solubility in water as a result of dispersion and sorption.

High-density organic liquids

The next case is similar to that just described, except that a small source within the bulk waste releases an or-



ganic liquid contaminant S (e.g., TCE), which is immiscible with and more dense than the groundwater. Liquid S is assumed to sink through the saturated zone as an immiscible phase, displacing the groundwater as it descends, as shown in Figure 1d. Some of the organic liquid is retained by capillary forces in the pores of the aquifer material. If the contaminant is slightly soluble in water, a plume develops by dissolution of the contaminant liquid retained in the aquifer pores as well as by dissolution of the pool of contaminant liquid residing on the bottom of the aquifer.

The resulting plume shape may be complex, depending on the speed of the organic liquid's descent and the amount retained in the aquifer pores. Note that the clay aquitard is assumed level and impervious to the contaminant liquid. Thus, there is no migration of the contaminant pool along the aquifer other than spreading. Figure 1d shows that the two deeper wells will be affected by the contaminant. Also note that the observed concentrations will rise to some value well below the contaminant's solubility. In addition, the contaminant concentration may remain relatively constant for long periods, even when the volume spilled does not seem particularly large from a practical standpoint (a few hundred or thousand gallons of slightly soluble organic liquid contaminants).

Transformable compounds

In a somewhat more complicated case, consider the simple sand–gravel hydrogeologic setting affected by several organic contaminants with different potentials for biotransformation. Assume the leachate from the bulk waste contains readily biodegradable organic solutes. Assume also that the resultant microbiological growth in the aquifer renders the traversed zone anaerobic, as shown by the nonsorbing tracer U in Figure 1e. The remainder of the saturated zone stays aerobic. A small source releases a low-density organic liquid F, which is slightly soluble. Once contaminant F is dissolved, it can be completely mineralized (transformed to carbon dioxide) under aerobic conditions, but it is not biotransformable under anaerobic conditions. Another small source releases an organic liquid "sinker" S, which is slightly soluble. The dissolved contaminant S is not transformable aerobically, but can be biotransformed under anaerobic conditions to an intermediate SS, which is more mobile than S and not readily degradable (for example, TCE transformed anaerobically to vinyl chloride).

In this case, contaminant F disappears from the aerobic zone above the leachate plume but persists within the plume. Conversely, contaminant S persists below the bulk leachate plume but disappears within the plume. Contaminant SS, which would not be found in the waste source itself, appears within the bulk waste leachate plume as a result of biotransformation. In this simplified portrayal no contaminants are observed in Well 1. Well 2 is affected by the bulk leachate plume U, the persistent portion of the F plume, and the transformation product SS. Well 3 is affected by contaminant S only.

Transport time scales

To illustrate the phenomena in a relatively clear and general fashion, the schematic diagrams in Figure 1 do not show specific time and distance scales. In fact, it is difficult to provide such scales with certainty because of the gaps in our understanding of the fundamental processes as they operate under natural conditions. However, if we take a situation that is sufficiently idealized to allow the application of a simple transport model, we can create and examine a quantitative illustration of the effects of advection, dispersion, and sorption.

We assume a sandy aquifer in which the average groundwater flow rate is 45 m/y, within the velocity range that is common. The aquifer is horizontal, unconfined, and has a 10-m-thick saturated zone as indicated in Figure 2a. There is an unlined waste burial pit that is 50 m wide (crossgradient) and a solvent tank buried in a 5-m-wide unlined vault immediately adjacent to it. The bottom of each (the aquifer and the pit) is very near the water table. The waste pit contains chloride ions (Cl^{2-}), TCE, and PCE, which leach continuously. The leachate contaminates the entire 10-m depth of the aquifer below the impoundment and results in an essentially constant and vertically uniform concentration of the contaminants at $x = 0$. We will assume, for simplicity, that the concentration of each is 1 ppm (1000 ppb) at $x = 0$; this is less than 0.1% and 1% of the solubilities of TCE and PCE, respectively.

We also will assume that simultaneous with the onset of contamination from the waste pit, a small spill occurs as the solvent tank is being filled, and 15 gal (57 L) of pure TCA sinks rapidly through the bottom of the vault, uniformly contaminating the saturated zone in an area 5 m wide. The liquid droplets of TCA in the aquifer then dissolve into the groundwater flowing by, and the TCA concentration reaches 500 ppm, approximately one-half its solubility, before dispersion and dilution begin beyond $x = 0$. Given the volume spilled, the area contaminated by the organic liquid, the initial concentration, the groundwater flow rate, and other typical aquifer characteristics, we calculate that complete dissolution of the TCA droplets takes approximately 10 weeks. It is worth noting, however, that dissolution times on the order of years can be calculated for industrial spills that would still be considered small (hundreds or thousands of gallons).

The dissolved contaminants migrate toward a monitoring well directly downgradient at a distance of 1000 m. Pumping the well during sampling is assumed to have a negligible effect on the gradient. We assume moderate dispersive characteristics for such migration distances in sandy aquifers: 10 m and 1 m for longitudinal and transverse horizontal dispersivity, respectively (*3*). Also we assume that the chloride ion is not retarded and the retardation factors for TCE, TCA, and PCE are 2, 2, and 3, respectively. Such retardation factors would be expected for transport of these solutes in a sandy aquifer of about 0.1% carbon content (*15*).

In this highly idealized case, we would expect the water quality history at the monitoring well to be that shown in Figure 2b. The vertical dashed line at about 22 years denotes the solute arrival time expected solely on the basis

of the average groundwater flow rate. However, the chloride concentration rises above a few ppb about five years earlier, owing to longitudinal dispersion. The chloride concentration rises slowly over 10–15 years to a plateau that is only 40–50% of the initial leachate concentration, because of horizontal transverse dispersion.

Figure 2b shows that their retardation causes TCE and PCE to arrive at later times. However, dispersion of the retarded contaminants results in considerable spreading of their fronts and their arrival at the well in significant concentrations 10 to 20 years before the average arrival times expected solely on the basis of the average flow rate and retardation factors (dashed lines at 44 and 66 years).

The combined effect of dispersion and sorption on the TCA pulse is dramatic. The maximum concentration observed at the well is approximately a factor of 2000 below the initial dissolved concentration in the spill zone. In addition, the dissolved TCA pulse, which resulted from 10 weeks' dissolution of the liquid TCA introduced into the aquifer, is detectable (above a few ppb) at the monitoring well for 20 to 30 years.

Because this example is fictitious, the results are useful only as illustrations of possible travel times, degrees of spreading, and so on. Nevertheless, several important implications are clear. Relatively small amounts of contaminant (tens of gallons of pure solvent) can be quite significant. The EPA has proposed a recommended limit of 200 ppb for TCA in drinking water. In this example a 15-gal spill would result in this limit (the horizontal line in Figure 2b) being exceeded for several years at the monitoring well. This example predicts that if only one such spill occurs every few years, the limit would be exceeded continuously once the first pulse of TCA reaches the well because the dispersing pulses would overlap.

Arrival times of retarded contaminants also cannot be estimated safely using only the average groundwater velocity and the retardation factor. This is particularly true for contaminants that cause concern at very low concentrations, such as TCE and PCE. If we assume a maximum acceptable concentration of 10–50 ppb, which is in the range currently under discussion, TCE and PCE would arrive at the monitoring well in our example about 9 and 13 years, respectively, before the expected average times. The arrivals would be even earlier if the aquifer's dispersive characteristics were greater than the rather moderate levels assumed.

Implications

It is clear that the appearance of pollutants in supply wells often follows their release to the subsurface by years, if not decades. Given the rapid expansion in the manufacture and use of synthetic organic chemicals since 1940, such time lags imply that contaminated wells will continue to be discovered at an increasing rate, even if improved handling and disposal practices prevent any new sources of contamination. Similarly, the onset of contamination at a supply well may mark the front of a set of overlapping plumes of different compounds advancing at different rates, which may affect the well in sequence for decades even if the original contaminant source is removed.

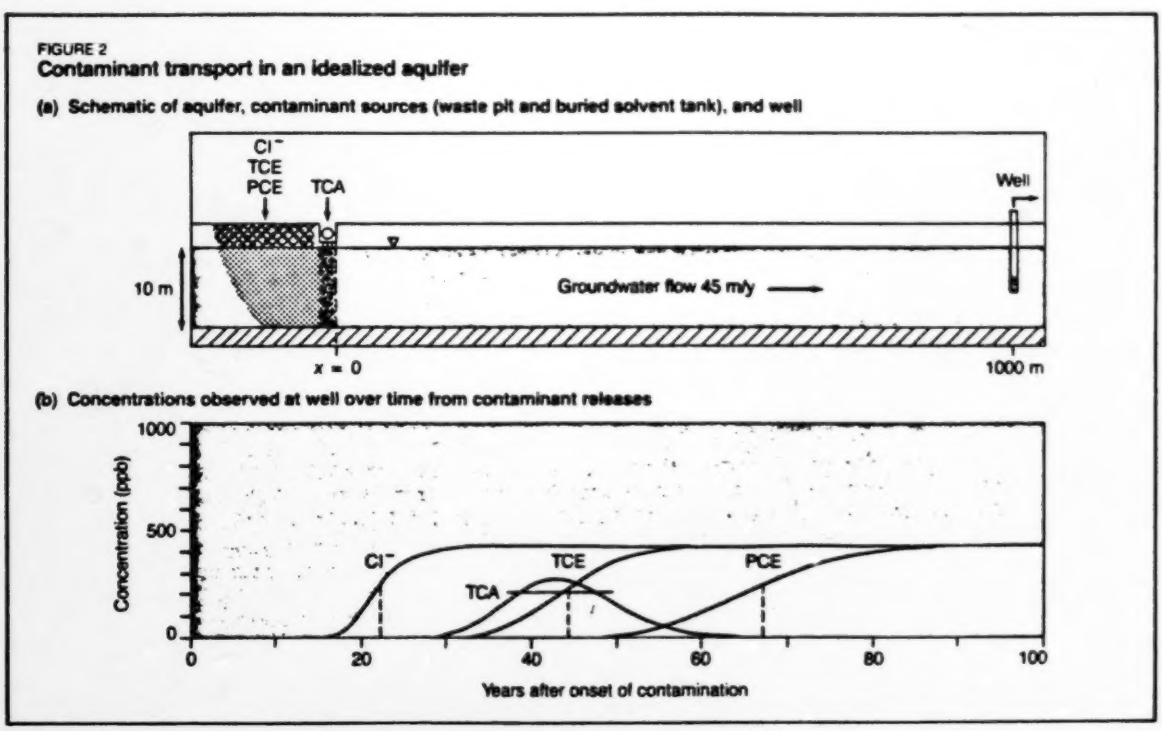
It is therefore imperative that we continue to seek greater understanding of the processes that control the transport and transformation of groundwater contaminants. As this knowledge grows, so will our ability to assess the present and future risks associated with groundwater contamination. Our ability to develop and choose wisely among alternatives for remediation will also increase.

In the following sections, some implications of our current understanding are discussed, highlighting areas of uncertainty to which research resources should be brought to bear.

Monitoring of complex sources

Consideration of the cases presented leads to the conclusion that the distribution of groundwater contaminants at waste disposal or industrial sites is likely to be complex. In each year of operation, landfills used for hazardous waste disposal are certain to have received hundreds or, more likely, thousands of small liquid sources (drums or tank-truck discharges) as well as thou-

FIGURE 2
Contaminant transport in an idealized aquifer



sands of loads of solid and semisolid wastes. It is therefore obvious that a given landfill will by no means contain a homogeneous mass of material.

Considering the areal extent of most landfills (from 5 to 200 hectares), the years elapsed during their filling, and the effect of the processes discussed above, it should be expected that the zone of subsurface contamination near unlined landfills on sandy aquifers cannot be delineated as a single plume. Rather the zone must be regarded as a multiplicity of plumes, superposed in three dimensions. Recent field studies support this contention and illustrate the error of assuming that the extent of organic contamination is enveloped by that of noninteractive tracers such as chloride (*26*). The distribution of subsurface contamination at industrial manufacturing sites also may be complex owing to a variety of contaminant sources such as dry wells, leaking pipes or storage tanks, surface impoundments, and inadvertent spills during chemical handling.

To predict the effect of future contamination near such complex sites, it would be ideal to have a detailed description of each source including the mass released, volume released, and period and area of release. More commonly, the available information is a limited set of observed pollutant concentrations at relatively few monitoring wells, often acquired years after release begins. Thus, the distribution must be deduced from the available data, which may have been obtained at different times with different sampling and analytical methods. Figures 1a–1e illustrate that if the number of reliable observations is limited, there is a high potential for misunderstanding the true contaminant distribution.

The problem is magnified if some or all of the observations from monitoring wells are misleading. The difficulties in obtaining useful and representative measurements of contaminant concentration and distribution have been discussed by a number of authors (*2, 27-29*). Such difficulties include wells located outside sample contaminant pathways (for example, Well 1 in Figures 1a, 1b, and 1d), wells that sample large depth intervals when contaminants are migrating in narrow vertical zones, and wells constructed of materials that alter the quality of the water being sampled. Sample collection, storage, and handling techniques that alter the quality of the sample and inappropriate or incomplete analytical methods also can give misleading information.

Predicting contaminant migration

In addition to descriptions of the contaminant sources, prediction of contaminant migration in the saturated zone requires quantitative representations of advection, dispersion, sorption, and transformation that are specific or at least applicable to the site, contaminants, and period of time in question. Available generalized models for the latter three processes have not yet been convincingly validated using field-scale observations or experiments in even simple sand and gravel aquifers. We must therefore acknowledge that predictions based on them will be uncertain to a degree that may be difficult to define. There is clearly a need for continued research to formulate improved process understanding in models that can be tested at both the laboratory and field scale.

Of particular interest are the interactions among different contaminants in superposed plumes, the rates and products of biotransformation, the effects of complex contaminant distributions on the activity of microorganisms, and the flow and dissolution of immiscible organic liquids. In addition, more resources must be applied to the understanding of contaminant transport and fate in the vadose zone and in heterogeneous hydrogeologic systems, such as discontinuous and interbedded layers of different geologic media and media that contain fractures caused by weathering or seismic activity.

We also need more information about the effects of human activities on the ability of aquitards to prevent vertical flow of contaminants to underlying aquifers. For example, there is evidence from laboratory studies that certain organic liquids can cause desiccation and cracking of unweathered clay, which lead to significant increases in permeability (*30, 31*). The importance of this effect in the natural environment is unknown. A more direct effect may be caused by abandoned or improperly installed wells that penetrate aquitards and provide rapid routes to the underlying aquifers. In Santa Clara (Silicon) Valley, Calif., for example, past agricultural activity has left a legacy to the current residential and high-technology industrial cohabitants of perhaps as many as 10,000 inactive and abandoned irrigation wells, the locations of which are largely unknown (*32*).

Evaluating remedial action

Remedial schemes designed to stop or reverse the spread of groundwater contaminants often rely on pumping the contaminated zone to purge it of contaminants (*33*). However, if the hydrogeologic situation and the processes that govern the transport of contaminants under natural groundwater flow are not well understood for a specific site, it may be difficult to predict with much confidence what will result from altering natural flow by use of groundwater extraction wells. The processes that disperse and retard the transport of the contaminants can be expected to increase significantly the time and volume of pumping required to decontaminate an area compared with what would be expected based solely on the aquifer volume occupied by the contaminant. The existence of even small volumes of immiscible organic liquids in the subsurface will provide reservoirs of the contaminant and perhaps greatly prolong the pumping time compared with that anticipated when assuming that only dissolved contaminants are present.

Although additional research on transport processes will certainly improve our ability to assess the probable effectiveness of remedial methods, current understanding seems to suggest that remediation based solely on pumping is likely to be a long and expensive undertaking. Pumping is an energy-intensive process and the extracted water may require costly treatment prior to discharge.

These concerns have led to the proposal and investigation of remedial schemes based on in situ biotransformation of contaminants, which may be relatively rapid and inexpensive com-

pared with years of pumping and treatment (*21*). Although the prospects appear encouraging for remediation by stimulating the activity of microorganisms native to soils and aquifers, much additional laboratory and field research is needed before these techniques can be applied on a practical and significant scale (*21*).

Conclusion

Understanding of contaminant transport in groundwater has improved greatly in recent years, especially since 1975, as public awareness has grown. We are acquiring a better grasp of the governing principles and have improved our ability to simulate, and in a very limited sense to predict, the movement of some classes of contaminants. Nevertheless, the problems at hand are complex, and there is clearly a need for much more detailed knowledge of the physical, chemical, and microbiological processes that control the fate and transport of contaminants in the subsurface environment.

Applying our conceptual understanding in a general fashion to typical hydrogeologic settings does help explain one perplexing aspect of hazardous chemical contamination: the time sequence of its development and recognition. The extreme time lags that characterize contaminant transport suggest that groundwater contamination by hazardous chemicals is a long-term problem that can reach large proportions before being recognized. It is a problem that is likely to persist long after serious mitigation efforts have begun. It is important to recognize that the time constants for water quality changes in groundwater are large, approaching those that characterize oceans and large lakes and much greater than those for streams.

These long transport times, typically measured in decades, are similar in magnitude to latency periods characterizing chronic health effects such as environmentally induced cancer. This sequence complicates the assessment of the potential for health problems that result from hazardous chemical contamination of subsurface drinking water supplies. Quantitation of health effects based on past exposures may be biased intrinsically toward underestimating the ultimate magnitude of the problem. One thing is certain, groundwater contamination will remain with us for many decades, even if efforts to control present and future emissions are largely successful.

Acknowledgment

Mark N. Goltz assisted in formulating and simulating the examples. Preparation of this paper was supported in part by the Life Sciences Research Office of the Federation of American Societies for Experimental Biology and the Universities Associated for Research and Education in Pathology. Although the information described in this article has been funded in part by the U.S. EPA under Assistance Agreement CR-808851 to Stanford University, it has not been subjected to the agency's required peer and administrative review and therefore does not necessarily reflect the views of the agency and no official endorsement should be inferred.

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***Douglas M. Mackay** is a research associate in environmental engineering at Stanford University. Since 1981 he has managed an interdisciplinary research project on groundwater contamination. He obtained B.S., M.S., and Ph.D. degrees from Stanford, the latter two in environmental engineering. From 1973 to 1975 he worked for EPA and recently collaborated with the agency on an assessment of risks from groundwater contamination in Santa Clara Valley, Calif.*

***Paul V. Roberts** (l.) is professor of environmental engineering at Stanford University. His educational background is in chemical engineering. After working as a research and design engineer at Chevron Research, SRI International, and the Swiss Federal Institute of Technology, he joined the Stanford University faculty in 1976. He has published some 100 papers on water pollution control, water treatment, and contaminant transport.*

***John A. Cherry** (r.) is a professor in the Department of Earth Sciences at the University of Waterloo, Ontario, a position he has held since 1971. His research focuses on migration processes and monitoring contaminants in groundwater.*

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